RATE CONSTANTS FOR THE REACTION OF OH RADICALS WITH CH_3CN, C_2H_5CN AND CH_2=CH–CN IN THE TEMPERATURE RANGE 298–424 K

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Rate constants for the reactions of OH with CH_3CN, CH_3CH_2CN and CH_2=CH–CN have been measured to be 5.86×10^{-13} exp(−1500 ± 250 cal mole^{-1}/RT), 2.69×10^{-13} exp(−1590 ± 350 cal mole^{-1}/RT) and 4.04×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively in the temperature range 298–424 K. These results are discussed in terms of the atmospheric lifetimes of nitriles.

1. Introduction

The formation of NO and NO_2 (NO_x) from molecular nitrogen in air during fossil-fuel combustion can be greatly reduced by appropriate modifications to combustion technology. On the other hand, the amount of NO_x produced from *fuel-bound* nitrogen is not much affected by these modifications. Hence the reduction of NO to N_2 by ammonia injection *after* combustion has been proposed as a method of controlling NO_x emission effectively, irrespective of the source of the nitrogen atoms.

Ammonia reduction methods based on both catalytic [1] and thermal [2] systems are under development, the latter being based on the fact that between 1000 and 1300 K, the reaction

$$NO + NH_3 + \tfrac{1}{4}O_2 \rightarrow N_2 + \tfrac{3}{2}H_2O \qquad (1)$$

is highly favored thermodynamically and completes very effectively with

$$NH_3 + \tfrac{5}{4}O_2 \rightarrow NO + \tfrac{3}{2}H_2O, \qquad (2)$$

leading to quantitative reduction of NO without "large" surviving NH_3 concentrations. Nonetheless, it is important to determine what concentrations of NH_3 would be emitted in a practical NO_x reduction system and whether complex free-radical reactions, especially involving hydrocarbons also present in the combustion exhaust gases, may lead to the formation of undesirable side products in the system.

A clue to possible side products formed under such conditions can be found in published studies of the ammoxidation (reaction with NH_3 in the presence of O_2) of unsaturated hydrocarbons over metal oxide catalysts at elevated temperatures. Thus, propene yields acrylonitrile and acetonitrile [3]; isobutene gave methacrylonitrile and acetonitrile [4] and the xylenes produced mixtures of difunctional aromatic nitriles and amides [5,6].

The work reported here provides kinetic information relevant to the atmospheric lifetimes of some of these potential nitrile side products, specifically acetonitrile, propionitrile and acrylonitrile. This information, aside from its fundamental interest, represents necessary data for the assessment of the air quality impact (and, especially in the case of acrylonitrile, the potential direct health impact) of increased emission of these compounds from controlled combustion and other sources.

2. Experimental

The apparatus and techniques used have been described previously [7] so only a brief description will be given here. Hydroxyl radicals are produced by the pulsed vacuum ultraviolet photolysis of H_2O at wave-

lengths $\lambda \geqslant 115$ nm (MgF_2 cut-off) and their concentration monitored as a function of time after the flash by resonance fluorescence. The reaction vessel is a Pyrex cylinder, 20 cm in length and 12 cm in diameter, fitted with two quartz windows at right angles to one another. The flash lamp is operated at discharge energies of 30–120 J per flash and repetition times of one flash every three seconds.

The OH resonance radiation is produced by a 2450 MHz microwave discharge through a flow of 3% H_2O in argon at ≈1 Torr total pressure. The radiation from the resonance lamp is focused into the reaction vessel at right angles to the flash beam. Resonance fluorescence from the hydroxyl radicals is observed at right angles to both the flash beam and the resonance radiation by a cooled EMI 9659QA photomultiplier tube fitted with an interference filter with a center wavelength of 308.9 nm and a half-bandwidth of 2.0 nm. This interference filter transmits mainly the 306.4 nm band of OH($a\,^2\Sigma^+, v' = 0 \rightarrow X\,^2\Pi, v'' = 0$). The intersection of the aperture of the detection system and the resonance radiation beam defines a fluorescence viewing zone of ≈2 cm cross section at the center of the reaction vessel. This region is well separated from the walls, thus minimizing wall losses of OH radicals. Signals are obtained by photon counting in conjunction with a Nuclear Data ND-2400 multichannel analyzer operated in the multichannel scaling mode.

The reaction cell is enclosed in a furnace, the temperature of which can be held constant to better than ±1 K over the temperature range 295–475 K, and the gas temperature is measured by a chromel/alumel thermocouple mounted inside the reaction vessel but clear of the fluorescence viewing zone.

All experiments were carried out under flow conditions so that the gas mixture in the reaction vessel was replenished every few flashes to avoid the accumulation of photolysis or reaction products and to minimize problems associated with adsorption of the reactants on the reaction vessel walls. The partial pressure of H_2O in the reaction cell typically ranges from 0.01 to 0.03 Torr. Reactant concentrations were controlled by saturating a known fraction of the Ar buffer gas flow with the nitrile at 298 K (CH_3CN and C_2H_5CN) or at 228 K (CH_2=CHCN). The reactant partial pressures in this fraction were measured by spectrophotometry in the IR or UV (CH_3CN: CN stretch at 2280 cm^{-1}, CH_3CH_2CN: CH stretch at 3010 cm^{-1} using a Perkin–Elmer 283 spectrometer; CH_2=CH–CN at 207 nm using a Cary 15 spectrophotometer). The system was calibrated by measuring the optical absorption of known pressures of the nitriles as determined by an MKS Baratron capacitance manometer. All gas flows were monitored with calibrated flow meters and the gases were premixed and thermally equilibrated before entering the reaction vessel.

3. Results

The reactions of OH radicals with acetonitrile, propionitrile and acrylonitrile were studied over the temperature range 298–424 K at typical total pressures of 50 Torr argon. Under the experimental conditions employed the pseudo-first-order decays of the OH radical concentrations following production in the flash are given by the integrated rate expression

$$[OH]_0/[OH]_t = S_0/S_t$$

$$= \exp\{(k_0 + k[\text{nitrile}])(t - t_0)\},$$

where $[OH]_0$ and $[OH]_t$, S_0 and S_t are the OH concentrations and resonance fluorescence signal intensities at times $t = 0$ and $t = t$, respectively; k_0 is the first-order removal rate constant for OH radicals in the absence of added reactant and is attributed primarily to diffusion of OH out of the viewing zone and to reaction with impurities; k is the rate constant for the reaction

OH + nitrile → products.

In all experiments, exponential decays of the reso-

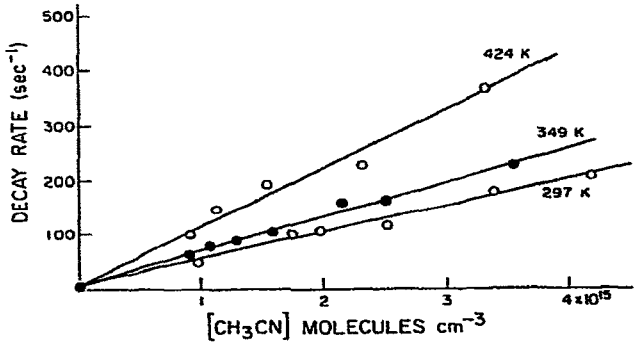

Fig. 1. Pseudo-first-order hydroxyl decay rates as a function of [CH_3CN] at three temperatures.

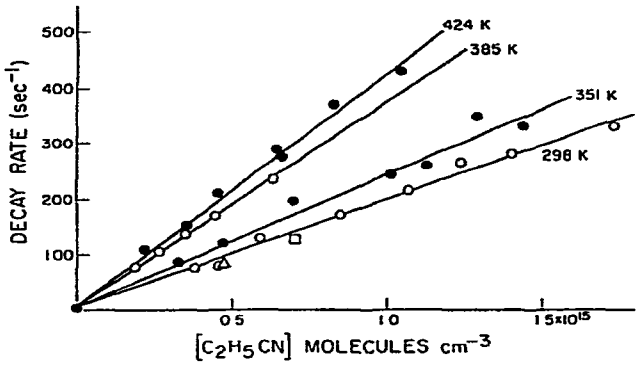

Fig. 2. Pseudo-first-order hydroxyl decay rates as a function of added $[C_2H_5CN]$ at four temperatures.

nance fluorescence signal were observed and the measured pseudo-first-order decay rates were found to depend linearly on the nitrile concentration.

Figs. 1–3 show plots of OH radical decay rates against reactant concentration for CH_3CN, C_2H_5CN and CH_2=CHCN, respectively, at the temperatures studied. In the case of the acetonitrile reaction, no significant variation of the rate constant for reaction with hydroxyl radicals was observed in the accessible temperature range and the data for all three temperatures studied at 50 Torr total pressure are fitted by the single line so labelled in fig. 3.

Table 1 lists the rate constants k obtained by least-squares analysis of the data in figs. 1–3. In the case of acrylonitrile, decay rates were also measured for T = 298 K at total pressures of 100 and 500 Torr argon. As can be seen from fig. 3 and table 1, the rate constant

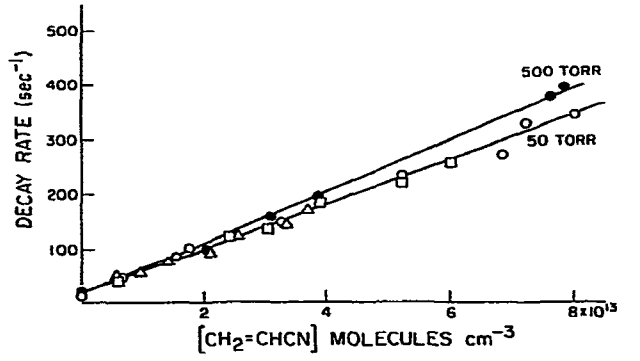

Fig. 3. Pseudo-first-order hydroxyl decay rates as a function of added $[CH_2$=CH–CN] for three temperatures at 50 Torr Ar total pressure [299 K (o), 350 K (△) and 423 K (□)] and at 299 K, 500 Torr total pressure (●).

Table 1
Rate constants for the reactions of OH radicals with acetonitrile, propionitrile and acrylonitrille [a]

Reactant	Temperature (K)	10^{13} k (cm^3 $molecule^{-1}$ s^{-1})
acetonitrile	297.2	0.494 ± 0.06
	348.0	0.620 ± 0.07
	423.8	1.05 ± 0.15
propionitrile	298.2	1.94 ± 0.20
	350.8	2 33 ± 0.25
	384.0	3.62 ± 0.36
	423.0	4.14 ± 0.40
acrylonitrile	299.0	40.6 ± 4.1
	349.6	40.4 ± 4.1
	422.5	40.2 ± 4.0
	298.7 [b]	43.2 ± 4.3
	298.7 [c]	48.0 ± 5.0

[a] The indicated error limits are the estimated overall error limits and include the least-squares standard deviations as well as the estimated accuracy limits of flow meter calibrations, pressure measurements, etc.
[b] Total pressure 100 Torr argon.
[c] Total pressure 500 Torr argon.

was ≈18% higher at the highest pressure, indicating that the reaction proceeds partially or entirely via an addition mechanism and that at room temperature the reaction is in its fall-off region between second-order and third-order kinetics in the pressure range studied.

The Arrhenius expressions obtained from least-squares analysis of the data in table 1 are in table 2,

Table 2
Arrhenius parameters for the reactions of OH radicals with acetonitrile, propionitrile and acrylonitrile [a]

Reactant	10^{13} A (cm^3 $molecule^{-1}$ s^{-1})	E (cal $mole^{-1}$)
acetonitrile	5.86	1500 ± 250
propionitrile	26.9	1590 ± 350
acrylonitrile	40.4 ± 0.45 [b]	–

[a] The indicated errors for the activation energies are the estimated overall error limits.
[b] 50 Torr total pressure argon. No observable temperature dependence.

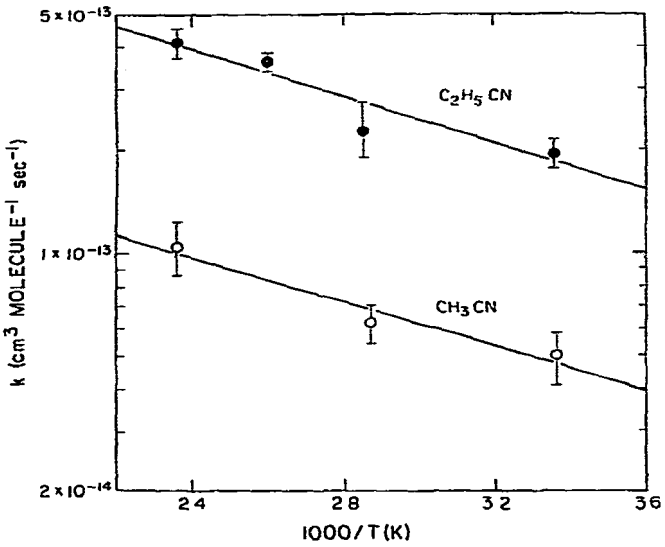

Fig. 4. Arrhenius plots for the reactions of OH with CH_3CN (○) and C_2H_5CN (●).

while fig. 4 shows the data for acetonitrile and propionitrile plotted in Arrhenius form. The error bars in fig. 4 represent three times the standard deviation of the slopes in figs. 1 and 2, but exclude possible systematic errors contributing to the estimated overall error listed in table 1.

4. Discussion

Variation of the flash energy by a factor of 2 and 4, and hence of the concentration of primary and secondary radicals by this amount, had no observable effect on rates of decay of hydroxyl radicals in our experiments, strongly suggesting that interference from secondary reactions, or from reactions of OH with products of the photolysis of the reactants, is negligible.

The rate constants for the reactions of OH radicals with acetonitrile and propionitrile exhibit Arrhenius activation energies of ≈1500 cal mole^{-1} which indicate that the reactions proceed largely or entirely by abstraction of a hydrogen atom. This conclusion is supported by the similarity of the measured rate constants for these reactions with those for the reactions of the analogous chloro-compounds CH_3Cl and CH_3CH_2Cl ($k^{298}_{CH_3Cl} = 4.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} [8], $k^{298}_{CH_3CH_2Cl} = 3.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [9] and by comparison with the very low rate constants in the range 10^{-15}–10^{-16} cm^3 molecule^{-1} s^{-1} measured by Phillips [10] for the reaction of OH with HCN.

Furthermore, the rates of the reactions of OH with CH_3CN and CH_3CH_2CN exhibit no dependence upon total pressure and hence the rate constants reported here are applicable to atmospheric pressure and may be used to calculate tropospheric destruction rates of the nitriles due to reaction with OH of ≈5×10^{-7} s^{-1} and ≈2×10^{-6} s^{-1}, respectively, for a mean concentration of OH of 10^7 radicals cm^{-3} and 298 K. Recent work in this laboratory indicates that the rates of reaction of these nitriles with ozone are slow ($k(O_3 + CH_3CN) \leqslant 1.5 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}; $k(O_3 + C_2H_5CN) \leqslant 1.0 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} [11]) and hence reaction with OH is the major homogeneous loss process for these nitriles; they will have lifetimes following release into a moderately polluted troposphere of ≈20 days and ≈6 days, respectively.

In the case of acrylonitrile, the measured rate constants are independent of temperature in the range studied and show a small (≈18%) increase over the range 50–500 Torr argon. The initial step in this reaction is therefore probably the addition of OH to the double bond, with the terminal site most likely being favored. A crude (but short) Lindemann-type extrapolation of the pressure-dependence data indicates that a value of $k_{CH_2=CHCN} = (4.9 \pm 0.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is appropriate for atmospheric modeling purposes, leading to a lifetime for acrylonitrile, in the presence of ≈10^7 [OH] cm^{-3}, of ≈5–6 h. The reaction of acrylonitrile with O_3 ($k \leqslant 1.0 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} [12]) is not sufficiently rapid to constitute a significant atmospheric sink.

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